

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 819 695 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
09.04.2003 Bulletin 2003/15

(51) Int Cl.7: **C07F 17/00**

(21) Application number: **97111446.7**

(22) Date of filing: **07.07.1997**

(54) **Process for modifying the rac/meso ratio in a metallocene compound**

Verfahren zur Modifikation von die Rac/Meso-Verhältnis einer Metallocenverbindung

Procédé pour la modification du rapport rac/meso d'un composé metallocène

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: **16.07.1996 EP 96202011**

(43) Date of publication of application:
21.01.1998 Bulletin 1998/04

(73) Proprietor: **Basell Polyolefine GmbH**
50389 Wessling (DE)

(72) Inventors:
• **Resconi, Luigi**
44100 Ferrara (IT)
• **Balboni, Davide**
44100 Ferrara (IT)

(74) Representative: **Colucci, Giuseppe et al**
Basell Poliolefine Italia S.p.A.,
Intellectual Property,
P.le G. Donegani 12
44100 Ferrara (IT)

(56) References cited:
WO-A-96/19488 **DE-A- 19 525 184**

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

EP 0 819 695 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a process for the modification of the rac/meso ratio of a rac/meso mixture in a stereorigid metallocene compound.

[0002] Stereorigid metallocene compounds having two substituted cyclopentadienyl ligands joined by means of a bridging group which gives stereo-rigidity to the molecule are known to be stereospecific catalyst components for the preparation of isotactic polyolefins. These metallocenes can exist in two configurations, that is the racemic and the meso isomeric form. As the chiral racemic form only is stereospecific, the meso form is generally removed by separation from the rac/meso mixtures obtained from the metallocene synthesis.

[0003] Thus, for example, in U.S. patent No. 4.769.510 it is described the use of rac-ethylene-bis(indenyl)zirconium dichloride and of rac-ethylene-bis(4,5,6,7-tetrahydroindenyl)-zirconium dichloride in combination with methylalumoxane for the preparation of isotactic polypropylene.

[0004] As regards the stereorigid metallocene compounds of the above type in their meso isomeric form, in EP-A-643,078 they are used in catalyst systems for the preparation of high molecular weight ethylene polymers.

[0005] Inasmuch as the methods for the preparation of the above metallocene compounds generally give a rac/meso mixture, both the racemic and the meso isomeric forms have to be separated from the corresponding undesired form. This is generally done by separation methods such as, for example, fractionated crystallization and extraction with solvents, which are often long, impractical and expensive. Moreover, the desired isomer is not always achievable with a high purity.

[0006] WO 95/35333 describes a process for the preparation of ethylene polymers having a broad molecular weight distribution by carrying out the polymerization reaction in the presence of a catalyst comprising a mixture of the racemic and meso isomers of a stereorigid metallocene compound and at least one co-catalyst capable of activating both the racemic form and the meso form of the metallocene compound. Different rac/meso ratios have been used in the working examples.

[0007] It is thus highly desirable to be able to prepare stereorigid metallocenes in their pure racemic or meso isomeric form, or in a rac/meso mixture with a fixed rac/meso ratio, without resorting to unpractical separation steps of the undesired isomer.

[0008] It has now unexpectedly been found that it is possible to selectively decompose one of the isomers of bridged chiral metallocenes in the presence of compounds having either acidic hydrogens or reactive halogen atoms.

[0009] Therefore, according to a first aspect, the present invention provides a process for the modification of the rac/meso ratio in a mixture of racemic and meso isomeric form of a stereorigid, bridged metallocene compound of a transition metal selected from those belonging to groups 3, 4, 5 or 6 or to the lanthanides or the actinides in the Periodic Table of the Elements (new IUPAC version), said process comprising contacting said mixture with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose at least part of one of the isomeric forms.

[0010] Depending on the type and concentration of the decomposition agent employed, as well as on the conditions in which the process is carried out, it is possible to control the degree of decomposition of the undesired isomer and, consequently, to prepare rac/meso mixtures enriched in one of the isomers or to prepare the desired isomer substantially free of the undesired isomer.

[0011] Inasmuch as the preparation of a stereorigid metallocene compound substantially free of one of its racemic or meso isomeric forms is particularly desirable, in an embodiment of the invention the conditions of the process are selected such that substantially all the undesired isomer is decomposed.

[0012] Therefore, according to another aspect, the present invention provides a process for the preparation of the racemic or meso isomeric form of a stereorigid, bridged metallocene compound of a transition metal selected from those belonging to groups 3, 4, 5 or 6 or to the lanthanides or the actinides in the Periodic Table of the Elements (new IUPAC version), said process comprising contacting a rac/meso isomeric mixture of the metallocene with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose substantially all the undesired isomer.

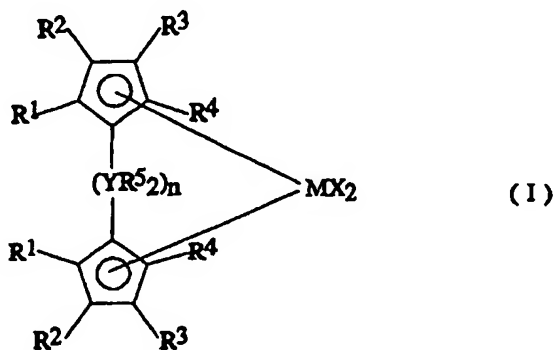
[0013] Non limitative examples of compounds having acidic hydrogen atoms which can be used in the process of the present invention are:

- water,
- alcohols such as methanol, ethanol and the like,
- organic and inorganic acids such as hydrochloric acid, acetic acid, p-toluen-sulphonic acid, HB(phenyl)_4 ,
- primary or secondary amines of the formula RNH_2 or R_2NH wherein R is an alkyl or aryl group such as diethylamine and the like,
- quaternary ammonium salts of the formula $(\text{R}_p\text{NH}^{4-p})_q(\text{X}^{q-})$, wherein p is 1, 2 or 3, n is 1 or 2, R is an alkyl group and X is a counteranion such as an halogen atom, a SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- or B(phenyl)_4^- group.

[0014] Non limitative examples of compounds having reactive halogen atoms which can be used in the process of the present invention are the chlorides such as those of the formula R'_3SiCl , R'_3GeCl or R'_3SnCl wherein R' is an alkyl group.

[0015] In order to reduce the time required for the decomposition, the above described decomposition agents are generally used in a molar ratio with the metal of the undesired metallocene isomer higher than 1:1.

[0016] A class of stereorigid, bridged metallocene compounds which are normally obtained as a rac/meso mixture and can thus be subjected to the process of the present invention are those of the formula (I):



wherein M is a metal selected from Ti, Zr and Hf;

the X substituents, same or different, are hydrogen atoms, halogen atoms or R, OR, SR, NR_2 or PR_2 groups, wherein the R substituents are C_1 - C_{20} -alkyl, C_3 - C_{20} -cycloalkyl, C_2 - C_{20} -alkenyl, C_6 - C_{20} -aryl, C_7 - C_{20} -alkylaryl or C_7 - C_{20} -arylalkyl radicals which can contain silicon or germanium atoms;

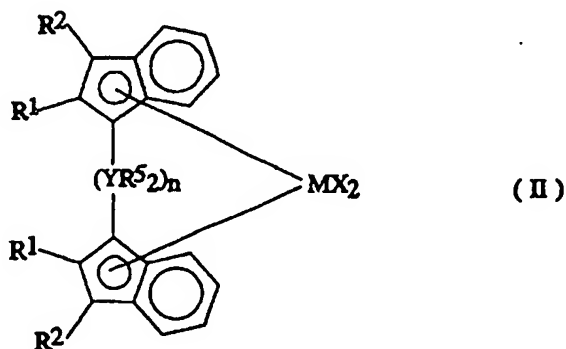
on each cyclopentadienyl group, the R^1 , R^2 , R^3 and R^4 substituents, same or different, are C_1 - C_{20} alkyl radicals, C_3 - C_{20} cycloalkyl radicals, C_2 - C_{20} alkenyl radicals, C_6 - C_{20} aryl radicals, C_7 - C_{20} alkylaryl radicals or C_7 - C_{20} arylalkyl radicals and can contain Si or Ge atoms, and moreover two of the R^1 , R^2 , R^3 and R^4 substituents adjacent on the same cyclopentadienyl ring can form a cycle comprising from 5 to 8 carbon atoms, with the proviso that, in at least one cyclopentadienyl group, R^1 is different from R^4 or R^2 is different from R^3 ;

Y is a carbon, silicon or germanium atom;

the R^5 substituents, same or different, are hydrogen atoms, C_1 - C_{20} alkyl radicals, C_3 - C_{20} cycloalkyl radicals, C_2 - C_{20} alkenyl radicals, C_6 - C_{20} aryl radicals, C_7 - C_{20} alkylaryl radicals or C_7 - C_{20} arylalkyl radicals, and moreover two substituents R^5 can form a cycle comprising from 4 to 8 carbon atoms;

n is an integer comprised between 1 and 4, preferably being 1 or 2.

[0017] A particularly interesting class of stereorigid, bridged metallocene compounds are the bridged bis-indenyl compounds of the formula (II):



and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds wherein R^1 , R^2 , R^5 , Y, n, M and X are defined as above, and the six-carbon-atom rings of the indenyl ligands can optionally be substituted.

[0018] Preferred metallocene compounds of the formulas (I) or (II) are those wherein M is Zr, the X substituents are chlorine atoms or methyl groups, the $(YR^5)_n$ bridging group is a CR^5_2 , SiR^5_2 or $(CR^5_2)_2$ group, more preferably a CH_2 , $C(CH_3)_2$, $Si(CH_3)_2$, or $(CH_2)_2$ group.

[0019] A particularly interesting metallocene compound is the ethylenebis(4,7-dimethyl-indenyl)zirconium dichloride which can be easily obtained in its pure meso isomeric form with the process of the present invention.

[0020] Therefore, according to a further aspect, the present invention provides a process for the preparation of ethylenebis(4,7-dimethyl-indenyl)zirconium dichloride in its substantially pure meso isomeric form, said process comprising contacting a rac/meso isomeric mixture of said metallocene with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose substantially all the racemic isomer.

[0021] A particularly convenient method for the synthesis of bridged metallocene compounds is described in European Patent Application EP 0 722 950. This method goes through the synthesis of intermediate silyl-, germyl- or stannyl-substituted ligands which can be prepared in their racemic and meso forms, and then can be selectively transformed into the corresponding metallocenes by reaction with a transition metal compound of formula MX_4 , wherein M is a titanium, zirconium or hafnium atom and X is an halogen atom.

[0022] It has been observed that if the rac/meso mixture of the silyl-, germyl- or stannyl- substituted ligand is allowed to react for prolonged times with the transition metal compound, one of the isomers is decomposed.

[0023] Therefore, according to a particularly suitable embodiment of the present invention, the decomposition agent is a silyl-, germyl- or stannyl-chloride of the formula R'_3SiCl , R'_3GeCl or R'_3SnCl , wherein R' is an alkyl group, which is generated by the reaction of a silyl-, germyl- or stannyl- substituted ligand of the target metallocene with a transition metal compound of formula MX_4 wherein M is a titanium, zirconium or hafnium atom, preferably a zirconium atom, and X is an halogen atom, preferably a chlorine atom.

[0024] The metallocene compounds obtainable with the process of the present invention are useable, in combination with a cocatalyst, in the polymerization of olefins.

[0025] The following examples are given for illustrative purposes and do not limit the invention.

CHARACTERIZATIONS

[0026] The 1H -NMR analyses were carried out on a Bruker 200 MHz instrument, using $CDCl_3$ as a solvent, at room temperature.

[0027] All the operations were carried out in a dry nitrogen atmosphere, using the conventional techniques for the handling of compounds which are sensitive to air.

THF = tetrahydrofuran

Et_2O = ethyl ether

Synthesis of 1,2-bis(1-trimethylsilyl-4,7-dimethyl-indenyl) ethane [EBDMI(TMS)₂]

[0028] 103.8 g (331 mmol) of 1,2-bis(4,7-dimethyl-indenyl)ethane (Boulder, mixture of double bonds positional isomers) were slurred in 680 mL of THF in a 1 L flask equipped with stirring bar. This suspension was added in small aliquots over 30 minutes at room temperature in a 2 L flask equipped with reflux condenser, thermometer and mechanical stirrer, containing 29.48 g of KH (735 mmol) and 205 mL of THF. The reaction was slightly exothermic (T max. 43 °C) with evolution of hydrogen. At the end of the addition the so obtained suspension was stirred for 2 h, obtaining a dark green solution. In a second 2 L flask equipped with thermometer, mechanical stirrer and dropping funnel were placed 93.2 mL of Me_3SiCl (734 mmol) and 210 mL of THF. The dark green solution of the potassium salt was added dropwise (2 h, slightly exothermic reaction, T max. 30 °C) and at the end of the addition the mixture was stirred for 44 h, obtaining a brown-orange milk. The reaction was monitored by NMR (40 mg dissolved in $CDCl_3$) and GC. After 16 h the reaction was complete. After 44 h the mixture was treated with water (200 mL) while stirring, and then NaCl to induce phase separation. The organic layer was dried over Na_2SO_4 , filtered and brought to dryness. 142.8 g of a light brown solid was obtained (yield 94.3%).

EXAMPLE 1 (Comparison)

Synthesis of rac/meso -ethylene-bis(4,7-dimethyl-indenyl) zirconium dichloride

[0029] 0.908 g of $ZrCl_4$ (PM 233.03 g/mol, 3.9 mmol), 90 mL of CH_2Cl_2 and 1.787 g of EBDMI(TMS)₂ (PM 458.5, 3.9 mmol) were placed in a 100 mL flask equipped with stirring bar. The dark brown suspension was stirred for 2 h, then the reaction stopped by removing all volatiles in vacuo: the brown powder was placed in a frit and washed several times with Et_2O until the Et_2O was light yellow (100 mL) then with CH_2Cl_2 and finally dried in vacuo. 0.638 g (35 %) of

yellow-orange powder were obtained: ^1H NMR shows the presence of a mixture of the two isomers of $\text{EBDMI}(\text{ZrCl}_2)$ (rac:meso = 45:55). The product was chemically pure.

EXAMPLE 2

Synthesis of meso-ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride

[0030] 0.75 g of ZrCl_4 (PM 233.03 g/mol, 3.22 mmol), 85 mL of CH_2Cl_2 and 1.47 g of $\text{EBDMI}(\text{TMS})_2$ (PM 458.5, 3.22 mmol) were charged in a 100 mL flask: a dark brown suspension was obtained which was stirred for 22 h at room temperature. 2 mL aliquots were taken out after 4 and 10 h. The aliquots were dried and analyzed by ^1H NMR. After 4 h the reaction was completed (all ligand consumed), with formation of a ca. 1:1 rac/meso with notable decomposition. After 10 h the racemic isomer was diminished, and decomposition increased. After 22 h the reaction was stopped by removing all volatiles in vacuo. The brown powder was transferred on a frit and washed with Et_2O (5×20 mL). After drying a yellow-green powder was obtained (0.364 g, 24 %) which analyzes (^1H NMR) as meso- $\text{EBDMI}(\text{ZrCl}_2)$ ($\geq 98\%$).

EXAMPLE 3

Synthesis of meso-ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride

[0031] 5.6 g of ZrCl_4 (PM 233.03 g/mol, 24 mmol), 220 mL of CH_2Cl_2 and 11 g of $\text{EBDMI}(\text{TMS})_2$ (PM 458.5, 24 mmol) were charged in a 250 mL flask equipped with stirring bar. A dark brown suspension was obtained, which was stirred at room temperature for 23 h. The reaction was stopped by filtration, and the residue was extracted with CH_2Cl_2 until colourless (the insoluble residue was discarded). The CH_2Cl_2 solutions were combined and brought to dryness under vacuum, yielding a brown powder which was placed in a frit and washed several times with Et_2O until the Et_2O was colourless (200 mL). A dark yellow powder was obtained. A fraction of it was washed with CH_2Cl_2 : ^1H NMR analysis revealed the presence of pure meso- $\text{EBDMI}(\text{ZrCl}_2)$ (the rac isomer being present in traces). The rest of the product contained, besides traces of the rac isomer, also some organic impurities: Et_2O alone was not enough to purify the product. Total yield 2.67 g, 24 %. The meso- $\text{EBDMI}(\text{ZrCl}_2)$ only was obtained, as a lemon yellow powder.

EXAMPLE 4

Synthesis of meso-ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride

[0032] 1.53 g of ZrCl_4 (PM 233.03 g/mol, 6.54 mmol), 100 mL of CH_2Cl_2 and 3 g of $\text{EBDMI}(\text{TMS})_2$ (PM 458.5, 6.54 mmol) were placed in a 250 mL flask equipped with stirring bar. The dark brown mixture was stirred 23 h at room temperature. The reaction was stopped by removing the volatiles under vacuum: the brown powder was placed in a frit and washed several times with Et_2O until the Et_2O was colourless (100 mL). A yellow-green powder (0.7 g, 23 %) was obtained, which contained meso- $\text{EBDMI}(\text{ZrCl}_2)$ (rac isomer traces) and organic impurities.

EXAMPLE 5

Meso-enrichment of a 1:1 rac/meso-mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride with H_2O

[0033] 0.25 g of a 1:1 rac/meso mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride were dissolved in 55 mL of THF in a 50 mL Schlenk tube under nitrogen, 47 microliters of water were added with a syringe ($\text{Zr}/\text{H}_2\text{O} = 5$ molar), and the solution was stirred for 4 hours. Half of the solution was taken out, dried at 30 °C for 5 hours. The solid product was analyzed by ^1H NMR (CDCl_3 , 200 Mhz): meso/rac ratio = 90:10. The rest of the solution was stirred for a total of 24 hours, and analyzed in the same way: meso/rac ratio = 100:0.

EXAMPLE 6

Meso-enrichment of a 1:1 rac/meso-mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride with CH_3OH

[0034] 0.25 g of a 1:1 rac/meso mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride were dissolved in 55 mL of CH_2Cl_2 in a 50 mL Schlenk tube under nitrogen, methanol was added with a syringe ($\text{Zr}/\text{CH}_3\text{OH} = 5$ molar), and the solution was stirred for 4 hours. Half of the solution was taken out, dried at 30 °C for 5 hours. The solid product was analyzed by ^1H NMR (CDCl_3 , 200 Mhz): meso/rac ratio = 60:40. The rest of the solution was stirred for a total of 24 hours, and analyzed in the same way: meso/rac ratio = 60:40.

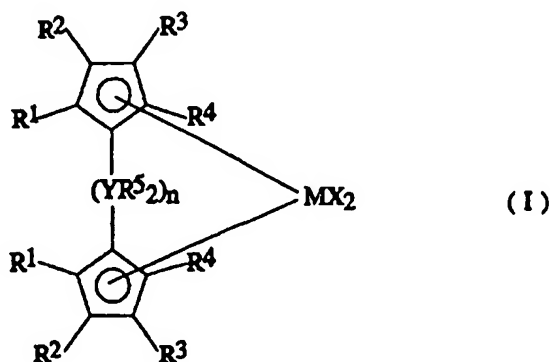
EXAMPLE 7

Meso-enrichment of a 1:1 *rac*/*meso*-mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride with $(\text{CH}_3)_3\text{SiCl}$

[0035] 0.25 g of a 1:1 *rac*/*meso* mixture of ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride were dissolved in 55 mL of CH_2Cl_2 in a 50 mL Schlenk tube under nitrogen, trimethylchlorosilane was added with a syringe ($\text{Zr}/(\text{CH}_3)_3\text{SiCl}$ = 5 molar), and the solution was stirred for 24 hours, and analyzed by ^1H NMR (CDCl_3 , 200 Mhz): *meso*/*rac* ratio = 2:1.

Claims

1. A process for the modification of the *rac*/*meso* ratio in a mixture of racemic and *meso* isomeric form of a stereorigid, bridged metallocene compound of a transition metal selected from those belonging to groups 3, 4, 5 or 6 or to the lanthanides or the actinides in the Periodic Table of the Elements (new IUPAC version), said process comprising contacting said mixture with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose at least part of one of the isomeric forms.
2. A process for the preparation of the racemic or *meso* isomeric form of a stereorigid, bridged metallocene compound of a transition metal selected from those belonging to groups 3, 4, 5 or 6 or to the lanthanides or the actinides in the Periodic Table of the Elements (new IUPAC version), said process comprising contacting a *rac*/*meso* isomeric mixture of the metallocene with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose substantially all the undesired isomer.
3. The process according to any of claims 1 or 2, wherein the compound having an acidic hydrogen atom is selected between:
 - water,
 - alcohols
 - organic and inorganic acids
 - primary or secondary amines of the formula RNH_2 or R_2NH wherein R is an alkyl or aryl group
 - quaternary ammonium salts of the formula $(\text{R}_p\text{NH}^+_{4-p})_q(\text{X}^q_-)$, wherein p is 1, 2 or 3, n is 1 or 2, R is an alkyl group and X is a counteranion such as an halogen atom, a SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- or $\text{B}(\text{phenyl})_4^-$ group.
4. The process according to any of claims 1 or 2, wherein the compound having a reactive halogen atom is selected from the chlorides of the formula $\text{R}'_3\text{SiCl}$, $\text{R}'_3\text{GeCl}$ or $\text{R}'_3\text{SnCl}$ wherein R' is an alkyl group.
5. The process according to any of claims 1 or 2, wherein the decomposition agent is used in a molar ratio with the metal of the undesired metallocene isomer higher than 1:1.
6. The process according to any of claims 1 or 2, wherein the metallocene compound is selected between those of the formula (I):



wherein M is a metal selected from Ti, Zr and Hf;

the X substituents, same or different, are hydrogen atoms, halogen atoms or R, OR, SR, NR₂ or PR₂ groups, wherein the R substituents are C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl radicals which can contain silicon or germanium atoms;

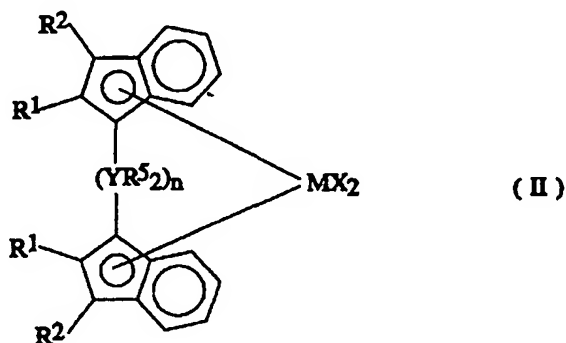
on each cyclopentadienyl group, the R¹, R², R³ and R⁴ substituents, same or different, are C₁-C₂₀ alkyl radicals, C₃-C₂₀ cycloalkyl radicals, C₂-C₂₀ alkenyl radicals, C₆-C₂₀ aryl radicals, C₇-C₂₀ alkylaryl radicals or C₇-C₂₀ arylalkyl radicals and can contain Si or Ge atoms, and moreover two of the R¹, R², R³ and R⁴ substituents adjacent on the same cyclopentadienyl ring can form a cycle comprising from 5 to 8 carbon atoms, with the proviso that, in at least one cyclopentadienyl group, R¹ is different from R⁴ or R² is different from R³;

Y is a carbon, silicon or germanium atom;

the R⁵ substituents, same or different, are hydrogen atoms, C₁-C₂₀ alkyl radicals, C₃-C₂₀ cycloalkyl radicals, C₂-C₂₀ alkenyl radicals, C₆-C₂₀ aryl radicals, C₇-C₂₀ alkylaryl radicals or C₇-C₂₀ arylalkyl radicals, and moreover two substituents R⁵ can form a cycle comprising from 4 to 8 carbon atoms;

n is an integer comprised between 1 and 4, preferably being 1 or 2.

7. The process according to claim 6, wherein the metallocene compound is selected between those of the formula (II):



and the corresponding bis-4,5,6,7-tetrahydroindenyl compounds wherein R¹, R², R⁵, Y, n, M and X are defined as in claim 6, and the six-carbon-atom rings of the indenyl ligands can optionally be substituted.

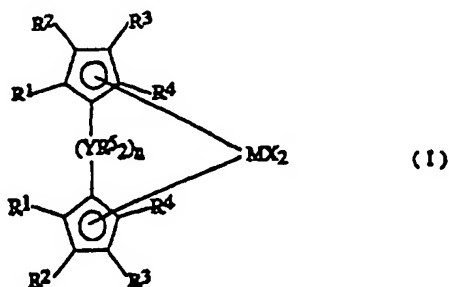
8. The process according to any of claims 6 or 7, wherein in the metallocene compounds of the formulas (I) or (II) M is Zr, the X substituents are chlorine atoms or methyl groups, the (YR⁵₂)_n bridging group is a CR⁵₂, SiR⁵₂ or (CR⁵₂)₂ group, preferably a CH₂, C(CH₃)₂, Si(CH₃)₂, or (CH₂)₂ group.
9. A process for the preparation of ethylenebis(4,7-dimethyl-indenyl)zirconium dichloride in its substantially pure meso isomeric form, said process comprising contacting a rac/meso isomeric mixture of said metallocene with a decomposition agent selected from the compounds having either an acidic hydrogen atom or a reactive halogen atom for a time sufficient to decompose substantially all the racemic isomer.
10. The process according to any of the preceding claims, wherein the decomposition agent is a silyl-, germyl- or stannyl-chloride of the formula R'₃SiCl, R'₃GeCl or R'₃SnCl, wherein R' is an alkyl group, which is generated by the reaction of a silyl-, germyl- or stannyl-substituted ligand of the target metallocene with a transition metal compound of formula MX₄ wherein M is a titanium, zirconium or hafnium atom, preferably a zirconium atom, and X is an halogen atom, preferably a chlorine atom.

Patentansprüche

1. Verfahren zur Modifizierung des rac/meso-Verhältnisses in einem Gemisch von racemischer und meso-Isomeren-Form einer stereorigiden verbrückten Metallocenverbindung eines Übergangsmetalls, ausgewählt aus jenen, die zu Gruppen 3, 4, 5 oder 6 oder zu den Lanthaniden oder den Actiniden des Periodensystems der Elemente (neue IUPAC-Version) gehören, wobei das Verfahren In-Kontakt-Bringen des Gemisches mit einem Zersetzungsmittel,

ausgewählt aus den Verbindungen mit entweder einem sauren Wasserstoffatom oder einem reaktiven Halogenatom, für einen zum Zersetzen von mindestens einem Teil von einer der isomeren Formen ausreichenden Zeitraum umfasst.

2. Verfahren zur Herstellung der racemischen oder meso-Isomeren-Form einer stereorigiden verbrückten Metallocenverbindung eines Übergangsmetalls, ausgewählt aus jenen, die zu Gruppen 3, 4, 5 oder 6 oder zu den Lanthaniden oder den Actiniden des Periodensystems der Elemente (neue IUPAC-Version) gehören, wobei das Verfahren In-Kontakt-Bringen eines rac/meso-Isomerengemisches des Metallocens mit einem Zersetzungsmittel, ausgewählt aus den Verbindungen mit entweder einem sauren Wasserstoffatom oder einem reaktiven Halogenatom, für einen ausreichenden Zeitraum zum Zersetzen im Wesentlichen des gesamten unerwünschten Isomers umfasst.
3. Verfahren nach einem der Ansprüche 1 oder 2, wobei die Verbindung mit einem sauren Wasserstoffatom ausgewählt ist, zwischen:
 - Wasser,
 - Alkoholen,
 - organischen und anorganischen Säuren,
 - primären oder sekundären Aminen der Formel RNH_2 oder R_2NH , worin R eine Alkyl- oder Arylgruppe darstellt,
 - quaternären Ammoniumsalzen der Formel $(R_pNH^+_{4-p})_q(X^q-)$, worin p 1, 2 oder 3 ist, n 1 oder 2 ist, R eine Alkylgruppe darstellt und X ein Gegenanion, wie ein Halogenatom, eine Gruppe SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- oder $B(Phenyl)_4^-$ darstellt.
4. Verfahren nach einem der Ansprüche 1 oder 2, wobei die Verbindung mit dem reaktiven Halogenatom ausgewählt ist aus den Chloriden der Formel R'_3SiCl , R'_3GeCl oder R'_3SnCl , worin R' eine Alkylgruppe darstellt.
5. Verfahren nach einem der Ansprüche 1 oder 2, wobei das Zersetzungsmittel mit dem Metall des unerwünschten Metallocenisomers in einem Molverhältnis höher als 1:1 vorliegt.
6. Verfahren nach einem der Ansprüche 1 oder 2, wobei die Metallocenverbindung ausgewählt ist zwischen jenen der Formel (I):



worin M ein Metall, ausgewählt aus Ti, Zr und Hf, darstellt;
 die Substituenten X gleich oder verschieden Wasserstoffatome, Halogenatome oder Gruppen R, OR, SR, NR_2 oder PR_2 darstellen, worin die Substituenten R C_1 - C_{20} -Alkyl-, C_3 - C_{20} -Cycloalkyl-, C_2 - C_{20} -Alkenyl-, C_6 - C_{20} -Aryl-, C_7 - C_{20} -Alkylaryl- oder C_7 - C_{20} -Arylalkylreste, die Silizium- oder Germaniumatome enthalten können, darstellen,

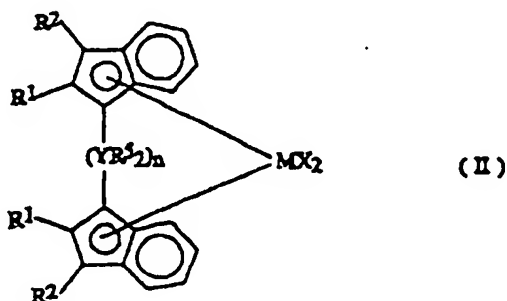
an jeder Cyclopentadienylgruppe die Substituenten R^1 , R^2 , R^3 und R^4 gleich oder verschieden C_1 - C_{20} -Alkylreste, C_3 - C_{20} -Cycloalkylreste, C_2 - C_{20} -Alkenylreste, C_6 - C_{20} -Arylreste, C_7 - C_{20} -Alkylarylreste oder C_7 - C_{20} -Arylalkylreste darstellen und S oder Ge-Atome enthalten können und darüber hinaus zwei der am gleichen Cyclopentadienylring benachbarten Substituenten R^1 , R^2 , R^3 und R^4 einen 5-8 Kohlenstoffatome umfassenden Cyclus bilden können, mit der Maßgabe, dass in mindestens einer Cyclopentadienylgruppe R^1 von R^4 verschieden ist oder R^2 von R^3 verschieden ist;

Y ein Kohlenstoff-, Silizium- oder Germaniumatom darstellt;

die Substituenten R^5 gleich oder verschieden Wasserstoffatome, C_1 - C_{20} -Alkylreste, C_3 - C_{20} -Cycloalkylreste,

C₂-C₂₀-Alkenylreste, C₆-C₂₀-Arylreste, C₇-C₂₀-Alkylarylreste oder C₇-C₂₀-Arylalkylreste darstellen und darüber hinaus 2 Substituenten R⁵ einen Cyclus, umfassend 4 bis 8 Kohlenstoffatome, bilden können;
n eine ganze Zahl umfasst zwischen 1 und 4, vorzugsweise 1 oder 2, ist.

7. Verfahren nach Anspruch 6, wobei die Metallocenverbindung zwischen jenen der Formel (II) :



und den entsprechenden Bis-4,5,6,7-tetrahydroindenylverbindungen, worin R¹, R², R⁵, Y, n, M und X wie in Anspruch 6 definiert sind, und die Sechs-Kohlenstoffatom-Ringe der Indenylliganden gegebenenfalls substituiert sein können, ausgewählt ist.

8. Verfahren nach einem der Ansprüche 6 oder 7, wobei in den Metallocenverbindungen der Formeln (I) oder (II) M Zr darstellt, die Substituenten X Chloratome oder Methylgruppen darstellen, die Brückengruppe (YR⁵)_n eine Gruppe CR⁵₂, SiR⁵₂ oder (CR⁵)₂, vorzugsweise eine Gruppe CH₂, C(CH₃)₂, Si(CH₃)₂ oder (CH₂)₂, darstellt.
9. Verfahren zur Herstellung von Ethylenbis(4,7-dimethyl-indenyl)zirkoniumdichlorid im Wesentlichen seiner reinen meso-Isomeren-Form, wobei das Verfahren In-Kontakt-Bringen eines rac/meso-Isomerengemisches des Metallocens mit einem Zersetzungsmittel, ausgewählt aus Verbindungen mit entweder einem sauren Wasserstoffatom oder einem reaktiven Halogenatom, für einen zum Zersetzen im Wesentlichen des gesamten racemischen Isomers ausreichenden Zeitraum umfasst.
10. Verfahren nach einem der vorangehenden Ansprüche, wobei das Zersetzungsmittel ein Silyl-, Germyl- oder Stannylchlorid der Formel R'₃SiCl, R'₃GeCl oder R'₃SnCl ist, worin R' eine Alkylgruppe darstellt, die durch die Reaktion eines Silyl-, Germyl- oder Stannyl-substituierten Liganden des Zielmetallocens mit einer Übergangsmetallverbindung der Formel MX₄, worin M ein Titan-, Zirkonium- oder Hafniumatom, vorzugsweise ein Zirkoniumatom, darstellt und X ein Halogenatom, vorzugsweise ein Chloratom, darstellt, erzeugt wird.

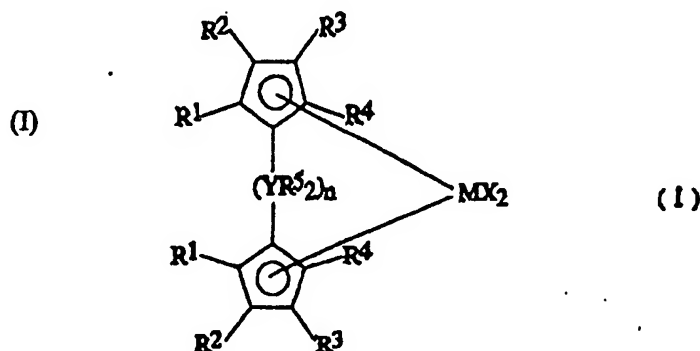
Revendications

1. Procédé pour la modification du rapport rac/mésomé dans un mélange de formes isomères racémique et méso d'un composé métallocène ponté stéréorigide d'un métal de transition choisi parmi ceux qui appartiennent aux groupes 3, 4, 5 ou 6 ou aux lanthanides ou aux actinides dans le Tableau Périodique des Éléments (nouvelle version IUPAC), ledit procédé comprenant la mise en contact dudit mélange avec un agent de décomposition choisi parmi les composés ayant soit un atome d'hydrogène acide, soit un atome d'halogène réactif pendant un temps suffisant pour décomposer au moins une partie de l'une des formes isomères.
2. Procédé pour la préparation de la forme isomère racémique ou méso d'un composé métallocène ponté stéréorigide d'un métal de transition choisi parmi ceux qui appartiennent aux groupes 3, 4, 5 ou 6 ou aux lanthanides ou aux actinides dans le Tableau Périodique des Éléments (nouvelle version IUPAC), ledit procédé comprenant la mise en contact d'un mélange isomère rac/mésomé du métallocène avec un agent de décomposition choisi parmi les composés ayant soit un atome d'hydrogène acide, soit un atome d'halogène réactif pendant un temps suffisant pour décomposer substantiellement la totalité de l'isomère indésiré.
3. Procédé suivant l'une quelconque des revendications 1 ou 2, dans lequel le composé ayant un atome d'hydrogène

acide est choisi parmi:

- l'eau,
- les alcools,
- les acides organiques et inorganiques,
- les amines primaires ou secondaires de formule RNH_2 ou R_2NH , dans lesquelles R est un groupe alkyle ou aryle,
- les sels d'ammonium quaternaire de formule $(R_pNH^{4-p})_q(X^{q-})$, dans laquelle p est 1, 2 ou 3, n est 1 ou 2, R est un groupe alkyle et X est un contre-anion comme un atome d'halogène, un groupe SO_4^{2-} , HSO_4^- , CO_3^{2-} , HCO_3^- ou B(phényl) 4^- .

4. Procédé suivant l'une quelconque des revendications 1 ou 2, dans lequel le composé ayant un atome d'halogène réactif est choisi parmi les chlorures de formule R'_3SiCl , R'_3GeCl ou R'_3SnCl dans laquelle R' est un groupe alkyle.
5. Procédé suivant l'une quelconque des revendications 1 ou 2, dans lequel l'agent de décomposition est utilisé selon un rapport molaire avec le métal de l'isomère indésiré de métallocène supérieur à 1:1.
6. Procédé suivant l'une quelconque des revendications 1 ou 2, dans lequel le composé métallocène est choisi parmi ceux de formule (I):



dans laquelle :

M est un métal choisi parmi Ti, Zr et Hf ;

les substituants X, identiques ou différents, sont des atomes d'hydrogène, des atomes d'halogène ou des groupes R, OR, SR, NR_2 ou PR_2 , dans lesquels les substituants R sont des groupes alkyle en C_{1-20} , cycloalkyle en C_{3-20} , alcényle en C_{2-20} , aryle en C_{6-20} , alkylaryle en C_{7-20} ou arylalkyle en C_{7-20} qui peuvent contenir des atomes de silicium ou de germanium ;

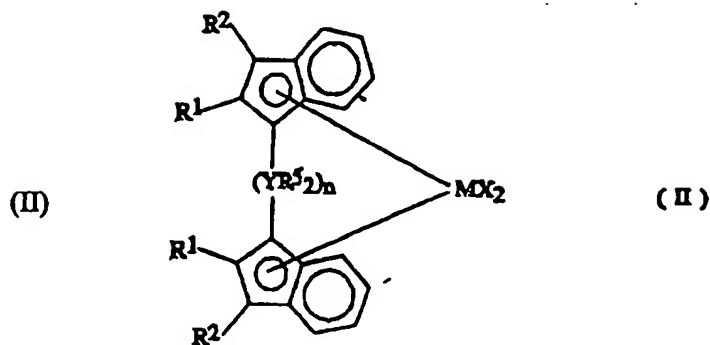
sur chaque groupe cyclopentadiényle, les substituants R^1 , R^2 , R^3 et R^4 , identiques ou différents, sont des groupes alkyle en C_{1-20} , des groupes cycloalkyle en C_{3-20} , des groupes alcényle en C_{2-20} , des groupes aryle en C_{6-20} , des groupes alkylaryle en C_{7-20} ou des groupes arylalkyle en C_{7-20} et peuvent contenir des atomes de silicium ou de germanium, et de plus, deux des substituants R^1 , R^2 , R^3 et R^4 adjacents sur le même cycle cyclopentadiényle peuvent former un cycle comprenant de 5 à 8 atomes de carbone, à la condition que dans au moins l'un des groupes cyclopentadiényle, R^1 soit différent de R^4 ou R^2 soit différent de R^3 ;

Y est un atome de carbone, de silicium ou de germanium ;

les substituants R^5 , identiques ou différents, sont des atomes d'hydrogène, des groupes alkyle en C_{1-20} , des groupes cycloalkyle en C_{3-20} , des groupes alcényle en C_{2-20} , des groupes aryle en C_{6-20} , des groupes alkylaryle en C_{7-20} ou des groupes arylalkyle en C_{7-20} , et de plus, deux substituants R^5 peuvent former un cycle comprenant de 4 à 8 atomes de carbone ;

n est un entier compris entre 1 et 4, de préférence n est 1 ou 2.

7. Procédé suivant la revendication 6, dans lequel le composé métallocène est choisi parmi ceux de formule (II):



et les composés bis-4,5,6,7-tétrahydroindényle correspondants, dans laquelle R^1 , R^2 , R^5 , Y, n, M et X sont tels que définis dans la revendication 6, et les noyaux à six atomes de carbone des ligands indényle peuvent être éventuellement substitués.

8. Procédé suivant l'une quelconque des revendications 6 ou 7, dans lequel, dans les composés métallocène des formules (I) ou (II), M est Zr, les substituants X sont des atomes de chlore ou des groupes méthyle, le groupe de pontage $(YR^5)_n$ est un groupe CR^5_2 , SiR^5_2 ou $(CR^5_2)_2$, de préférence un groupe CH_2 , $C(CH_3)_2$, $Si(CH_3)_2$ ou $(CH_2)_2$.
9. Procédé pour la préparation du dichlorure d'éthylène bis-(4,7-diméthyl-indényl)-zirconium sous sa forme isomère méso pratiquement pure, ledit procédé comprenant la mise en contact d'un mélange isomère rac/méso dudit métallocène avec un agent de décomposition choisi parmi les composés ayant soit un atome d'hydrogène acide, soit un atome d'halogène réactif pendant un temps suffisant pour décomposer substantiellement la totalité de l'isomère racémique.
10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'agent de décomposition est un chlorure de silyle, de germyle ou de stannyle de formule R'_3SiCl , R'_3GeCl ou R'_3SnCl , dans laquelle R' est un groupe alkyle, qui est généré par la réaction d'un ligand silyle- substitué par un germyle- ou stannyle- du métallocène cible avec un composé de métal de transition de formule MX_4 , dans laquelle M est un atome de titane, de zirconium ou de hafnium, de préférence un atome de zirconium, et X est un atome d'halogène, de préférence un atome de chlore.